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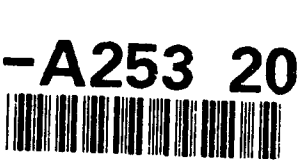

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Mobility of Toluene in Polystyrene-Toluene Solutions. A NMR Study.

by

Byaprorn naNagara, Robert D. O'Connor, and Frank D. Blum

Department of Chemistry and Materials Research Center
University of Missouri-Rolla
Rolla, MO 65401

(314) 341-4451

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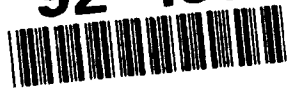

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Byaporn naNagara, Robert D. O'Connor, Frank D. Blum

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University of Missouri-Rolla
Department of Chemistry
Rolla, MO 65401
ATTN: Frank D. Blum
314-341-4451

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ABSTRACT

Self-diffusion coefficients, longitudinal (T_1) and transverse (T_2) NMR relaxation times of toluene in polystyrene-toluene solutions were determined at concentrations up to 50% polymer at room temperature to ca. -70°C. The self-diffusion coefficients were used to calculate the fraction of motionally-altered toluene based on deviations from the Maxwell-Fricke approximation of the obstruction effect. The fraction of motionally-altered toluene was found to be nearly constant with temperature for the lower polymer concentrations, but increased with decreasing temperature for the higher polymer concentrations. The relaxation times of the motionally-altered toluene were calculated using the two-fraction fast-exchange model and used to estimate the mean correlation times from a log-normal distribution of correlation times. The dependence of correlation times on temperature was found to be of the Arrhenius type and the activation energies increased with polymer concentration. The activation energies for translational diffusion ranged from 12 to 22 kJ/mol and those of the motionally altered solvent's rotational motion from 11 to 42 kJ/mol.

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INTRODUCTION

The motion of small molecules (rotational and translational) in polymer solutions is important in industrial, medical and biological applications. A few examples of these applications are: control of polymerization, drying of coatings, plasticization of polymers, controlled drug delivery, and membrane separations. There are a variety of methods for the determination of mutual and self-diffusion coefficients including sorption, permeation, dynamic light scattering, radioactive tracers, and nuclear magnetic resonance (NMR). The various methods for measuring diffusion coefficients have been reviewed[1] as well as the methods particularly useful for polymer-solvent systems.[2] For the investigation of molecular motions, NMR has proven to be a powerful tool because it is relatively non-perturbative. Even with the use of an isotope such as deuterium, the perturbation is still relatively small, even though phase separation of perdeuterated polymers sometimes occurs.[3]

Molecular motion can be studied using NMR with a variety of measurements including relaxation times or diffusion coefficients. For a deuterium nucleus in a C-D bond, NMR relaxation occurs mainly via the nuclear electric quadrupole interaction. NMR relaxation measurements yield information mostly on the rotational motion of molecules. Due to the absence of background deuterons and their inherently short relaxation times, specifically labelled samples can be used as very effective probes of molecular motion. The relaxation processes include the return to the spin thermal equilibrium described by the longitudinal relaxation time, T_1, and the decay of magnetization in the x-y plane described by the transverse relaxation time, T_2. While both relaxation times are sensitive to short-range (fast) motions, T_2 is also sensitive to long-range (slow) motions. The measurement of self-diffusion coefficients by nuclear magnetic resonance requires a magnetic-field gradient which is used to assign a spatial tag to the molecules via the Larmor precessional frequencies. The pulsed-gradient spin-echo (PGSE) NMR technique is usually employed for these measurements. Reviews of the PGSE technique,[4,5,6] and its

application to polymeric systems[4,7,8] have been published.

A significant number of studies have been directed toward an understanding of the dynamics of water in biopolymer systems[9-11] and in synthetic polymers.[12-15] However, there are comparatively fewer detailed studies of other solvents in polymer solutions. Water in biological macromolecule solutions is generally thought of as being divided into bound and free fractions in order to explain the decreases in relaxation times relative to pure water. Several models have been proposed for the molecular dynamics of bound water. Rorschach et al.[16] demonstrated that the orientational relaxation time of solute macromolecules (which results from rotational Brownian motion) is conveyed to the solvent molecules, and is detectable in their translation of water along the surface of proteins. Hallenga and Koenig[17] proposed a model of isotropic motion. Schauer[18] proposed that the Brownian motion of the macromolecules induces a hydrodynamic flow in bulk water.

In the present study, we have investigated the molecular dynamics of the solvent (toluene and toluene-d_8) in polystyrene (PS) solutions using NMR. The polystyrene-toluene system was chosen because most of the critical data and parameters needed for the interpretation of the results are available. The system is simpler than water-protein systems as there is neither hydrogen bonding nor pH effects on solvent-solute interactions. In addition, the diffusion[19-21] limited NMR relaxation[22] and solvent reorientation from Rayleigh-Brillouin spectra[23] of toluene in this system has been studied at other concentration and temperature ranges. The reported experiments were done at room temperature and below with concentrations up to 50% polymer where T_1 and T_2 differ enough to yield complementary information. In addition to the diffusion-coefficient measurements, the relaxation behavior has been probed to give a fuller view of both the translational and rotational dynamics of toluene.

MATERIALS AND METHODS

Atactic polystyrene (PS) from Pressure Chemical Company, Pittsburgh, PA. (M_n = 600,000, M_w/M_n = 1.10) was used as received. The samples were prepared by adding weighed amounts of PS (dried under vacuum) in either distilled toluene or toluene-d_8 (both from Aldrich Chemical Co., Milwaukee, WI). The protonated solvent was used for the diffusion measurements and the deuterated solvent for the relaxation studies.

The NMR diffusion measurements were run on a JEOL FX-100 spectrometer operating at 100 MHz for protons. The pulsed-field gradient spin-echo (PGSE) technique[4,5] was used with the homospoil accessory which produced a magnetic field gradient of ca. 0.06 T/m. This was determined from PGSE measurements on neat cyclohexane, assuming a self-diffusion coefficient of 1.475 x 10^{-9} m^2/sec at 25°C.[24] A JEOL temperature controller was used to control the temperature to within ± 2 °C. The spectra were taken using a 1000 Hz window, 4096 points and a pulse delay of 8 seconds. The standard deviations of the diffusion coefficients were taken from the standard deviations of the slopes of the weighted-least squares fits. In all of the range studied, this was less than 6%. The accuracy of measurements were estimated to be within 10% of the reported value.

The relaxation measurements were made on a Varian VXR-200 operating at 30.7 MHz for deuterons. For the T_1 and T_2 measurements, the standard inversion recovery (IR) and spin-echo (CPMG)[25] sequences were employed using software supplied by Varian Associates which included exponential fits of the data. The temperatures were controlled to within ± 2 °C by the thermoregulator supplied by Varian. For sub-ambient measurements a home-built N_2(l) evaporator was used for cooling. Typical spectra for T_1 and T_2 measurements were taken with a 1000 Hz window, 8192 points and a pulse delay of at least $4T_1$. The error percentages were similar to those of diffusion.

For self-diffusion studies, the pulse sequence of Stejskal and Tanner[26] yields an echo amplitude which is given by:[4,5,26,27]

$$A = A_0 f(\Delta) \exp\left(\frac{-2\Delta}{T_2} - (\gamma\delta G)^2 D(\Delta-\delta/3)\right) \quad (1)$$

where A denotes the peak intensities of the species being measured, A_0 is the signal intensity with $\delta = 0$, $f(\Delta)$ represents the contribution from J-modulation effects, Δ is the time between radio frequency pulses, T_2 is the transverse relaxation time, G is the gradient strength (T/m), γ is the magnetogyric ratio of the nucleus, δ is the field gradient pulse duration, and D is the self-diffusion coefficient. Equation (1) shows that the T_2 of the nucleus in question affects the intensity of the echo through the exponential term. The modification described by Stilbs[28] allows the time between RF pulses, Δ, to be kept constant throughout the experiment. In addition, with the appropriate choice of Δ the J-modulation effects[27] can be eliminated or at least reduced. The above equation can then be reduced to:

$$A = C_0(\Delta) \exp\left(- (\gamma\delta G)^2 D(\Delta-\delta/3)\right) \quad (2)$$

where C_0 is a constant factor for fixed Δ containing the other terms in equation 1. This allows D to be probed independently of T_2, but we remind the reader that the value of $C_0(\Delta)$ is dependent on, and often limited by, the T_2 of the nucleus under study. D is obtained from the slope of ln(A) vs $\delta^2(\Delta-\delta/3)$ for a known field gradient strength. All self-diffusion coefficients were calculated using a weighted least-squares method.[29]

The bulk T_1 and T_2's used in the motionally altered calculation were taken from the

exponetial fit to the experimental values. Log-normal fits to the T_1 and T_2 data were obtained using IMSL's numerical integration and non-linear minimization routines.

RESULTS

In all samples and at all temperatures studied, the time dependence of the intensities for each data set (diffusion, T_1 and T_2) were characterized by single-exponential decays. This means that on the time scale of the NMR experiment in this study, the exchange between different environments of toluene in polymer solution was fast (faster than several milliseconds). Thus the information about the dynamics for different environments is averaged by the mole fraction in each environment. Under these conditions, the NMR experiment cannot probe the environment of the different species separately.

The temperature dependence of the self-diffusion coefficients of toluene in polystyrene solutions from 0-50% are shown in Figure 1. The diffusion data for pure toluene agrees well with that previously reported.[30] The diffusion behavior appears to be Arrhenius-like and is represented by straight lines on the semi-log plot. A small amount of curvature is noted, but not deemed significant based on previous measurements.[21] The activation energies were calculated and tabulated in Table I. In general, a systematic increase in the energy of activation was found with increasing polymer concentration, consistent with our previous results at higher temperatures.[21]

The temperature dependence of the longitudinal (T_1) and tranverse relaxation times (T_2) of the aromatic resonance of toluene-d_8 are shown in Figures 2 and 3. The temperature dependence of both relaxation times show some curvature, but seem to be reasonably represented by Arrhenius behavior over much of the range studied. The lines drawn on the plots represent the linear best fits and are drawn in part to aid the eye. The results of T_1 and T_2 for pure toluene agree well with previous studies.[31, 32, 33] The activation energies for pure toluene for T_1[aromatic], T_2[aromatic], T_1[methyl], and T_2[methyl] were determined to be 10.2, 10.6, 7.5, and 7.8 kJ/mol, respectively. Rößler[32] found activation energies for toluene-d_5 and toluene-d_3 at the same temperature range for both T_1 and T_2 to be 9.0 kJ/mol, while Wilbur and Jonas[33] found the activation energy of the

methyl group slightly lower than that of aromatic group.

Although the T_1 behavior in polymer solutions appears linear in a semi-log plot with 1/T, at higher concentrations upward curvature associated with the vicinity of the T_1 minimum is observed. This curvature will distort the estimations of the energy of activation from T_1 measurements which consequently are not reported. At the T_1 minimum, the average correlation time of the solvent is approximately equal to the Larmor frequency (31 MHz).[25] For all of the data reported here, the mobility of toluene is clearly on the "fast" correlation time side of the T_1 minimum. The T_2 measurements do not suffer as severely from curvature in this range and so we have estimated apparent energies of activation from them. We recognize that the dynamic situation may be too complicated for a simple Arrhenius activation analysis, but for comparison only, the activation energies for the T_2's are also shown in Table I. The apparent activation energies calculated for the T_2's are typically larger than those for diffusion, especially at higher concentration.

The temperature dependence of both relaxation times of the methyl resonances are shown in Figures 4 and 5. The plots show some curvature especially at low temperatures. The curves are drawn to aid the eye. Some non-linearity occurs because the methyl group has two distinct modes of motion each with its own rotational correlation time.[34] The curvature is more pronounced in T_2 than T_1, further complicating the interpretation of both relaxation times. Because of these complicating factors, the energies of activation for this group are not reported.

DISCUSSION

The review of solvent diffusion in polymer gels by Muhr and Blanshard[35] summarizes the influence of the polymer on solvent self-diffusion in four ways: the obstruction effect, increased hydrodynamic drag, alteration of solvent properties, and polymer involvement (e.g. solvent molecules are trapped in cages of polymers). The diffusion of the solvent in polymer solutions is also assumed to be affected by the same influences. Because the molecular motion of the solvent is much faster than that of the polymer, the polymer appears relatively fixed on the time scale of the solvent. For example, for a solution of 11% polystyrene-d in toluene the deuteron T_1 and T_2 at room temperature was 3.63 and 2.75 ms, respectively.[36] This is more than two orders of magnitude shorter than the relaxation times of the solvent under similar conditions and corresponds to almost three orders of magnitude in mobility[36] (vide infra). In addition, work on swollen cross-linked polystyrene beads confirms this assumption as the diffusion rate in the cross-linked polymer beads is not significantly affected by the presence of cross-links and is mainly determined by the concentration of solvent in the bead.[37] Work in this laboratory[38,19] as well as others[39,40] confirm that to a first approximation the diffusion of the solvent in polymer solutions, in the concentration range studied here, depends chiefly on the polymer concentration and not on the chemical nature of the solvent. An exception to this has been noted for chlorinated biphenyls (Aroclor) used as solvents for various polymers.[41,42] For polybutadiene, the solvent motional rates are actually increased with the addition of polymer. This behavior was attributed to the "clustering" of the solvents due to the presence of certain polymers.[41,42]

The usual independence of the solvent diffusion on the nature of the chemical species suggests that the obstruction effect may be significant in the reduction of the solvent diffusion coefficient, but not necessarily the only effect. Simple mixture theories, which relate the transport properties of bulk suspensions to those of the continuous and dispersed phases, can be used as a

model for this system even though it is a solution. Many mixtu e relations have been employed to interpret the diffusion data in polymer solutions[13, 43, 44] and in gels.[45, 46] Deviations from the predicted values of the mixture theories have always been found in solutions and have usually been interpreted as resulting from an amount of non- (or at least slowly-) diffusing species surrounding the polymer. The basic assumption is that the transport of the polymer, combined with the "motionally-altered" solvent[47] is negligible compared with the surrounding "bulk-like" (bl) solvent. An excluded volume, which includes the volume of the polymer plus that of the motionally-altered solvent can be used in the mixture theory calculations.

Of the many mixture relationships that have been proposed, we employ Maxwell's[48] as described by Fricke[49] which has been used in the calculation of both the amount of motionally-altered solvent and the obstruction effect.[13,50] From the Maxwell-Fricke mixture relation, the self-diffusion coefficient of the solvent in solution, D, relative to that of the neat solvent, D_0, is given by:[13]

$$(1 - \phi_p)\frac{D}{D_0} = \frac{(1 - p)}{(1 + p/2)} \qquad (3)$$

where ϕ_p is the volume fraction of the polymer (volume of impenetrable species) and p is the volume fraction of polymer plus any motionally-altered solvent, i.e. $p = \phi_p + \phi_{ma}$. This assumes that the self-diffusion coefficient of any motionally-altered solvent is negligible. The left side of the equation includes a correction $(1-\phi_p)$ to adjust the data for the different reference volumes of the measurements as required by Fick's laws.[51, 52] We note that the diffusion results are also consistent with an interpretation based on free volumes,[21] however, we have not pursued this approach here.

The Maxwell-Fricke mixture theory was derived for use in predicting electrical conductivity

and permeability. It has good success in predicting transport properties in colloidal dispersions. In particular, it has been used to predict the diffusion coefficients of solvent in the presence of colloidal silica.[50,43] These particles were on the order of 200 Å and the diffusion was dominated by obstruction rather than surface effects.[50] As a first approximation, we assume that this functional form adequately describes the obstruction effect for the polymer segments.

In relaxation studies of the solvent in a polymer system, the two-fraction fast-exchange model (TFFE)[53, 54] has been employed to interpret the data in either polymer solutions[55] and/or gels.[56, 57] This model assumes that there are two states of solvent molecules, one which is next to the polymer (motionally-altered fraction) and the other which behaves like bulk solvent, i.e. "bulk-like". The model also assumes that rapid exchange occurs between the different states so that only one relaxation time or diffusion coefficient for the solvent results. Rapid exchange means that the exchange occurs on a time scale which is much shorter than the frequency differences (chemical shifts) of each site. The observed relaxation rates, which are the reciprocals of the relaxation times, are a population-weighted average of the different relaxation rates.[53, 54] This yields:

$$\frac{1}{T_{obs}} = \frac{F_{bl}}{T_{bl}} + \frac{F_{ma}}{T_{ma}} \qquad (4)$$

where the T's can be either T_1 or T_2. T_{obs} represents the observed relaxation time values of the solvent in polymer solution, and T_{bl} and T_{ma} are the relaxation times of bulk-like (assumed to be the same as pure solvent) and motionally-altered solvent, respectively. F_{bl} and F_{ma} are the bulk-like and motionally-altered fractions of solvent, respectively ($F_{ma} + F_{bl} = 1$). In terms of the overall volume fraction $\phi_{bl} + \phi_{ma} + \phi_p = 1$. In this model, the overall process is assumed to be "stationary" in the sense that the number of solvent molecules in each of the two states is constant

during the observation time and rapid exchange between the two states occurs.

The two-state model oversimplifies a complex situation where a variety of solvent environments exist. The assignment of one of the states to free solvent most likely overestimates its mobility and therefore the mobility determined for the motionally-altered state is probably slower than the actual value. There is, however, some basis for the use of the two-state model. Woessner and Snowden have measured NMR relaxation times of water in agar gel[58] and swellable clay[59] and determined that the variation in relaxation times with water content was consistent with a two state model in which the restricted water consisted of one or two molecular layers. This analysis has also been extended to the quadrupole splitting in lamellar liquid crystals with similar results.[60] Applying this treatment to non-hydrogen bonding systems would assumes that dispersive interactions and free volume effects are enough to partition the system. Altered relaxation times themselves would justify this assumption.

Even though the polymer is more flexible than either the silica or surfactant in the liquid crystal, it is still about 3 orders of magnitude slower in motion than bulk solvent.[36] The mobility of the polymer segments also decreases with increases in the concentration of polymer. At room temperature, the diffusion coefficient of toluene in an 80% polystyrene solution is at least two orders of magnitude lower than that of the pure solvent.[21] In terms of our model, all the toluene at this concentration would be motionally-altered. In more dilute solutions, the differences would be reduced, but it is difficult to estimate by how much.

In the two state model, the measured diffusion coefficient is the superposition of the diffusion coefficients in both environments weighted by their mole fractions. The important assumption made here is that the diffusion coefficient of the motionally altered species is negligible compared to that of the free species. Estimates of water diffusion near silica surfaces are from one to three orders of magnitude slower than bulk water.[61,62] Rotational mobility of water on silica and clay surfaces, exclusive of hydrogen exchange, is estimated to be 5 to 10 times slower than

bulk.[59, 63] It is noted that these are fairly rigid surfaces. Diffusion in 10 Å layers of smectic liquid crystals is still 1.5 orders of magnitude slower than bulk water.[64]

From the Maxwell-Fricke relation (eq. 3) and the measured self-diffusion coefficients, the motionally-altered fraction of toluene (F_{ma}) was calculated by solving for p. The motionally-altered fractions calculated by this method are shown in Figure 6. In this calculation, the volume fraction of polystyrene was calculated from its specific volume[65] at different temperatures. The volume fraction of toluene was calculated from its density as a function of temperature.[66] Ideal volumes of mixing were assumed because the error introduced by not using the actual values was small compared to that due to the assumptions implicit in the model. It is clearly seen from Figure 6 that at low concentrations of PS (5% and 11% PS), there are only small changes in bound fraction of toluene for all temperatures while at concentrations of 19%-25% PS the changes in bound fractions are significant at lower temperatures. At 40% and 50% PS the changes in bound fraction with temperature are almost linear within this temperature range. At low concentrations, the measurements are not very sensitive to the bound fraction and consequently have large experimental errors.

If one assumes that the motionally-altered fractions of solvent to which the diffusion and relaxation time measurements are sensitive are the same, then it is possible to use equation 4 to estimate the relaxation times of the motionally-altered solvents. In order to reduce the effect of experimental error, particularly at lower concentrations of polymer, we have used the "smoothed" values for motionally-altered fractions shown as the continuous curves in Figure 6. Figures 7-10 show the temperature dependence of T_1 and T_2 for motionally-altered solvent calculated from equation 4. The activation energy for the motionally-altered component of the aromatic T_2 is shown in Table I.

Of fundamental interest to solvent dynamics are the correlation times for molecular motion.

In principle these can be obtained from T_1 and T_2 measurements through the use of an appropriate model for molecular motion. It is of interest to determine the correlation times of motionally-altered toluene and how it changes with temperature and concentration. For nuclear magnetic relaxation of deuterium nuclei directly bonded to carbon atoms, the electric quadrupole interaction is the dominant mechanism. Since the principal electric field gradient can be taken as being nearly axially symmetric along the C-D bond vector, the T_1 and T_2 values are given by:[67]

$$\frac{1}{T_1} = \frac{3\pi^2}{20}\left(\frac{e^2qQ}{h}\right)^2\left[J(\omega_0) + 4J(2\omega_0)\right] \tag{5}$$

and

$$\frac{1}{T_2} = \frac{3\pi^2}{40}\left(\frac{e^2qQ}{h}\right)^2\left[3J(0) + 5J(\omega_0) + 2J(2\omega_0)\right] \tag{6}$$

where e^2qQ/h is the quadrupole coupling constant, $J(\omega)$ is the spectral density at frequency ω, and ω_0 is the Larmor frequency. For the C-D bonds in toluene, the quadrupole coupling constant is taken to be equal to 1.93×10^5 Hz and 1.65×10^5 Hz for the aromatic and methyl groups, respectively.[31] The spectral density function $J(\omega)$ is the Fourier transform of the autocorrelation function G(t) or

$$J(\omega) = \int_{-\infty}^{+\infty} G(t)\, e^{-i\omega t}\, dt \tag{7}$$

When the molecule reorients by isotropic rotational diffusion, the spectral density $J(\omega)$ takes the familiar form:[67]

$$J(\omega) = \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \tag{8}$$

where τ_c is the rotational correlation time. In the extreme narrowing limit, $(\omega\tau_c)^2 \ll 1$, T_1 should equal T_2. In this limit, T_1 and T_2 are given by:

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 \tau_c \tag{9}$$

In agreement with other investigators,[31] for pure toluene at our temperatures T_1 equals T_2 and equation 9 applies. However, T_1 does not equal to T_2 for the motionally altered solvent. Its motion is coupled to the polymer's and the fast isotropic model is inadequate. This coupling is apparent since the relaxation rates change with polymer concentration as do the modes of polymer motion. A similar coupling between segmental motions of polymer backbones and solvent self-diffusion has previously been suggested based on a free-volume treatment.[68] Many models used to analyze data of polymer relaxation have been reviewed and tested.[69-72] Since a wide variety of segmental motions and solvent environments are possible and with no further knowledge of the detailed molecular motion, it would appear resonable to invoke a distribution of correlation times. Thus, we used an empirical log-normal distribution which is similar in shape to the log χ^2 used by Schaefer,[73] but converges more rapidly and reflects the true mean rotational correlation time.[74]

For this model the spectral density can be taken as:[74]

$$J(\omega) = \int_0^{\infty} \frac{2\,\tau_0\,G(\tau)\,d\tau}{\left(1+\omega^2\,\tau_0{}^2\,\tau^2\right)} \tag{10}$$

where $G(\tau)$ is the density function and is given by:

$$G(\tau) = \frac{1}{\sqrt{\pi}\,\sigma\,\tau}\exp\left(\frac{-(ln(\tau)+\frac{\sigma^2}{4})^2}{\sigma^2}\right) \tag{11}$$

where σ is an adjustable width parameter, and τ_0 is the mean correlation time. The two parameters (σ and τ_0) are chosen to fit the T_1 and T_2 data.

The results of the data fitted with the log-normal model for τ_0 are shown in Figure 11. Only the aromatic peak is used to obtain the correlation times, as the correlation times of methyls are complicated by internal rotation.[31, 34] All the data could be fit by variations of σ and τ_0. Values of σ ranged from 3 to 5 except when T_1 approached T_2 in which case σ approached 0 and the distribution function became a delta function. Generally, σ decreased with decreasing polymer concentration or increasing temperature. This is consistent with the view that the motion is becoming more isotropic and/or faster with these changes.

Assumming Arrhenius behavior for the mean correlation time, τ_0, the activation energies for both the isotropic (using the average of T_1 and T_2) and distribution models are tabulated in Table I. For both, the activation energies increase with increases in polymer concentration. However, since the distributions cover several orders of magnitude and are skewed towards longer times, the

distribution model naturally results in higher energies. The true activation energy is most likely somewhere between the two models. Our average for the 50% polystyrene solution is 42 kJ/mol. For comparison, the activation energy of the backbone deuteron of polystyrene (58.7% PS in PS-toluene solution) calculated from T_1 measurements was 40 kJ/mol[32] Similarly, in comparable conditions the correlation times of the motionally altered solvent lies between that of the polymer (10^{-10}-10^{-8}) [75,76] and those of pure toluene. These two results are indicative of a polymer-solvent correlation.

The actual magnitude of apparent activation energies from a simple Arrhenius relationship may be questionable. However, as the polymer concentration increases both the decreasing mobility of the motionally-altered solvent (increased τ_0 values) and the increase in slow motion relaxation processes (large T_1/T_2 ratios) are consistent with coupling of the solvent's rotation to the polymer's motion. The actual mechanism for this coupling is still unknown. It is also important to note that Rayleigh-Brillouin spectroscopy suggests changes in toluene mobility with concentration (from 0-15% polymer) to be much smaller.[23] The reasons for this discrepency are not fully known, although this study suggests that below 15% polymer, the amount of motionally-altered toluene is small enough that it may be difficult to extract from experimental uncertainty.

CONCLUSION

A simple model has been used to obtain the values of relaxation and correlation times of toluene which is motionally altered because of the presence of the polymer. The amounts of motionally-altered solvent were calculated based on the reduction of the solvent self-diffusion coefficient from that predicted using obstruction theories. The log-normal distribution of correlation times was used to interpret the relaxation data for the motionally-altered solvent. The temperature and concentration dependence of correlation times for the motionally altered species seems physically realistic. For all quantities measured, the energies of activation increase as the polymer concentration increases, indicating a correlation between polymer and solvent motion. The energies of activation for diffusion are less than those from T_2 measurements and significantly less than those from the log-normal correlation times. Comparing the rate of change in the diffusion coefficients at high polymer concentration, where the majority of solvent is motionally altered, to that of the T_2 values leads us to conclude that the rotation of the motionally-altered solvent is more hindered than the overall translational motion. Though it is difficult to prove the validity of the model used, it seems to be a reasonable approximation to a very complicated problem.

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Registry Nos. Polystyrene, 9003-53-6;

Toluene, 108-88-3;

Toluene-d_8, 1861-00-3;

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(47) The term motionally-altered as used here applies to the solvent molecules which are just neighboring the polymer segments. It is tempting to use the term bound, but this suggests specific chemical binding which may or may not be present. The presence of a relatively slow polymer segment must alter the motion of a neighboring solvent via a viscous-drag effect. Within the framework of a simple two-state model, bulk-like and motionally-altered solvent are used here to describe the two states.

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Table I. Apparent activation energies of toluene (kJ/mol) from different measurements[a]

%PS	Diffusion	T_2(arom)	T_{2ma}(arom)	τ_c iso	τ_0 dist
0	11.8	10.6	10.6	10.4	11.0
5	12.1	13.1	16.8	15.9	17.3
11	12.9	16.3	18.4	17.5	20.2
19	14.4	20.2	20.2	18.6	23.6
25	15.5	23.7	22.5	20.3	26.7
33	17.6	26.5	25.2	22.3	30.4
40	19.4	33.0	31.5	25.1	38.9
50	22.5	43.1	41.8	30.6	52.1

arom = aromatic species

ma = motionally altered

iso = from isotropic model using motionally altered T_1 and T_2 data

dist = from log-normal distribution model using motionally altered T_1 and T_2 data

Figure Captions

Figure 1. Self-diffusion coefficients of toluene as a function of temperature and polystyrene concentration.

Figure 2. T_1 values of the toluene aromatic deuterons as a function of temperature and polystyrene concentration.

Figure 3. T_2 values of the toluene aromatic deuterons as a function of temperature and polystyrene concentration.

Figure 4. T_1 values of the toluene methyl deuterons as a function of temperature and polystyrene concentration

Figure 5. T_2 values of the toluene methyl deuterons as a function of temperature and polystyrene concentration.

Figure 6. Fraction of motionally-altered toluene calculated from the self-diffusion coefficients and obstruction effects as a function of temperature and polystyrene concentration. The curves drawn are from simple polynomial fits to the data.

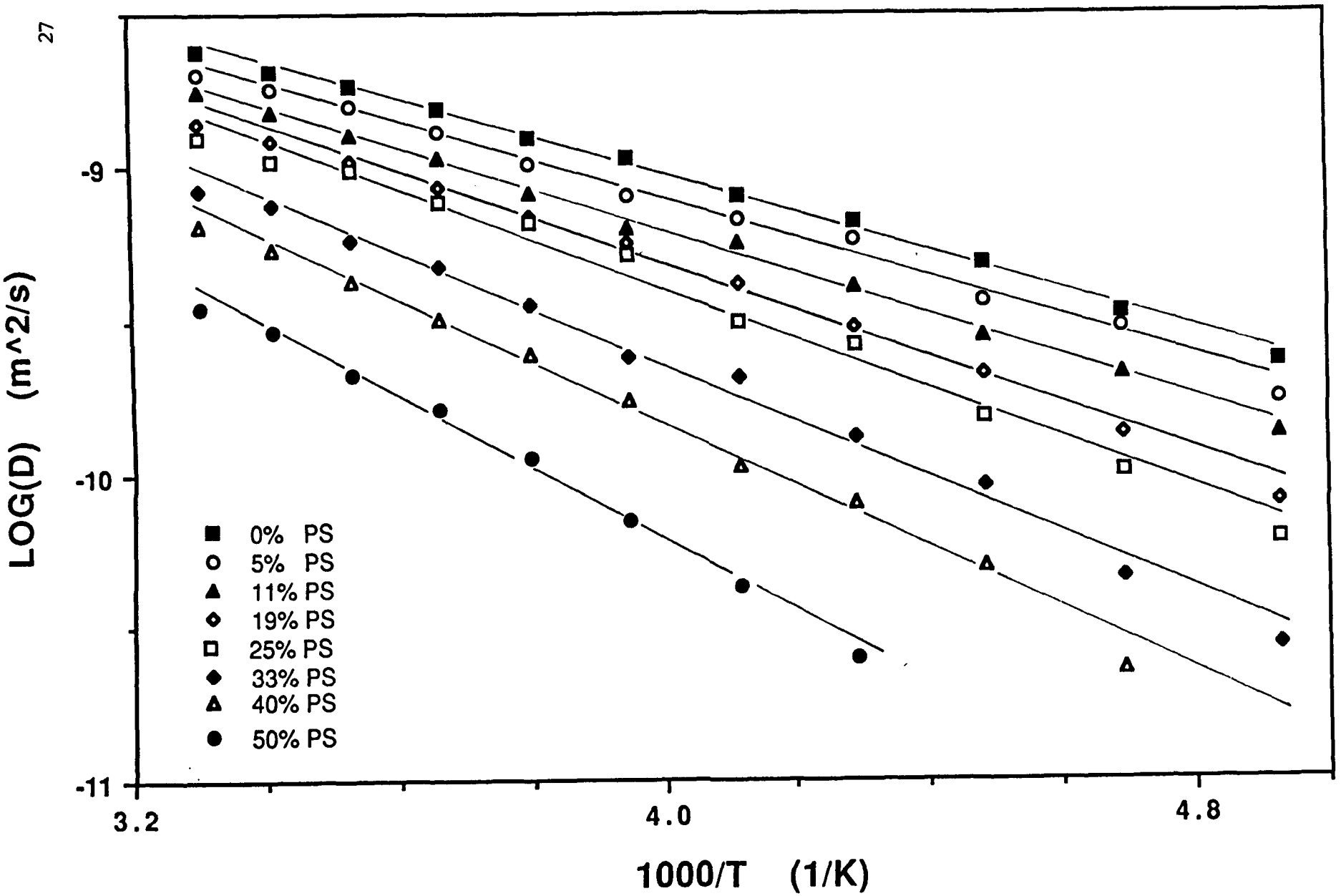
Figure 7. Plots of T_1 values of motionally-altered toluene (aromatic resonance) as a function of temperature and polystyrene concentration.

Figure 8. Plots of T_2 values of motionally-altered toluene (aromatic resonance) as a function of temperature and polystyrene concentration.

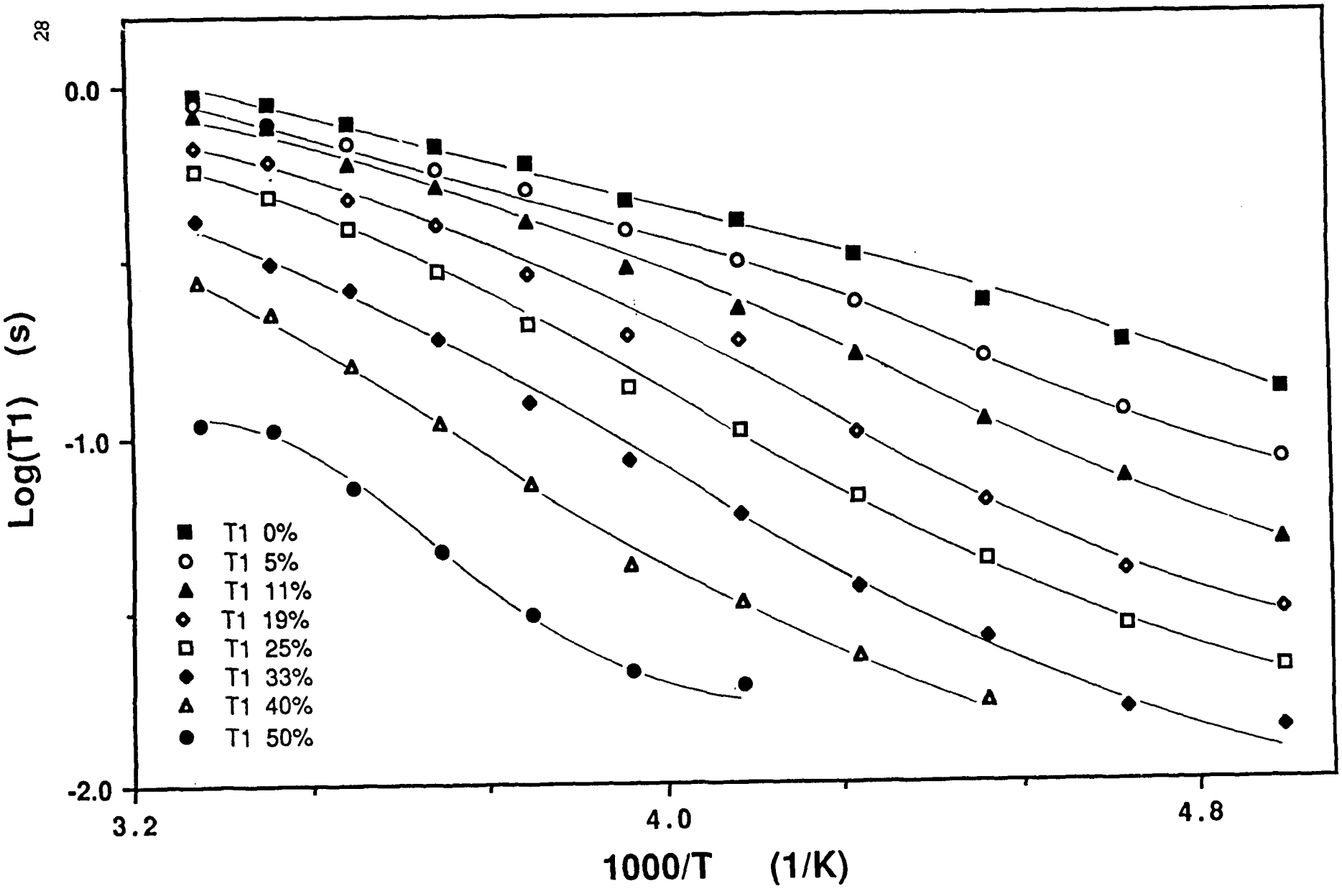
Figure 9. Plots of T_1 values of motionally-altered toluene (methyl resonance) as a function of temperature and polystyrene concentration (5% and 11% omitted for clarity).

Figure 10. Plots of T_2 values of motionally-altered toluene (methyl resonance) as a function of temperature and polystyrene concentration (5% and 11% omitted for clarity).

Figure 11. Plots of mean correlation time, τ_0, from the log-normal distribution as a function of temperature and polystyrene concentration (some data omitted for clarity).


LOG(D) (m^2/s)
-9
-10
-11
3.2
4.0
4.8
1000/T (1/K)
0% PS
5% PS
11% PS
19% PS
25% PS
33% PS
40% PS
50% PS

Before Fig 1


0.0
-1.0
-2.0
Log(T1) (s)
3.2
4.0
4.8
1000/T (1/K)
T1 0%
T1 5%
T1 11%
T1 19%
T1 25%
T1 33%
T1 40%
T1 50%

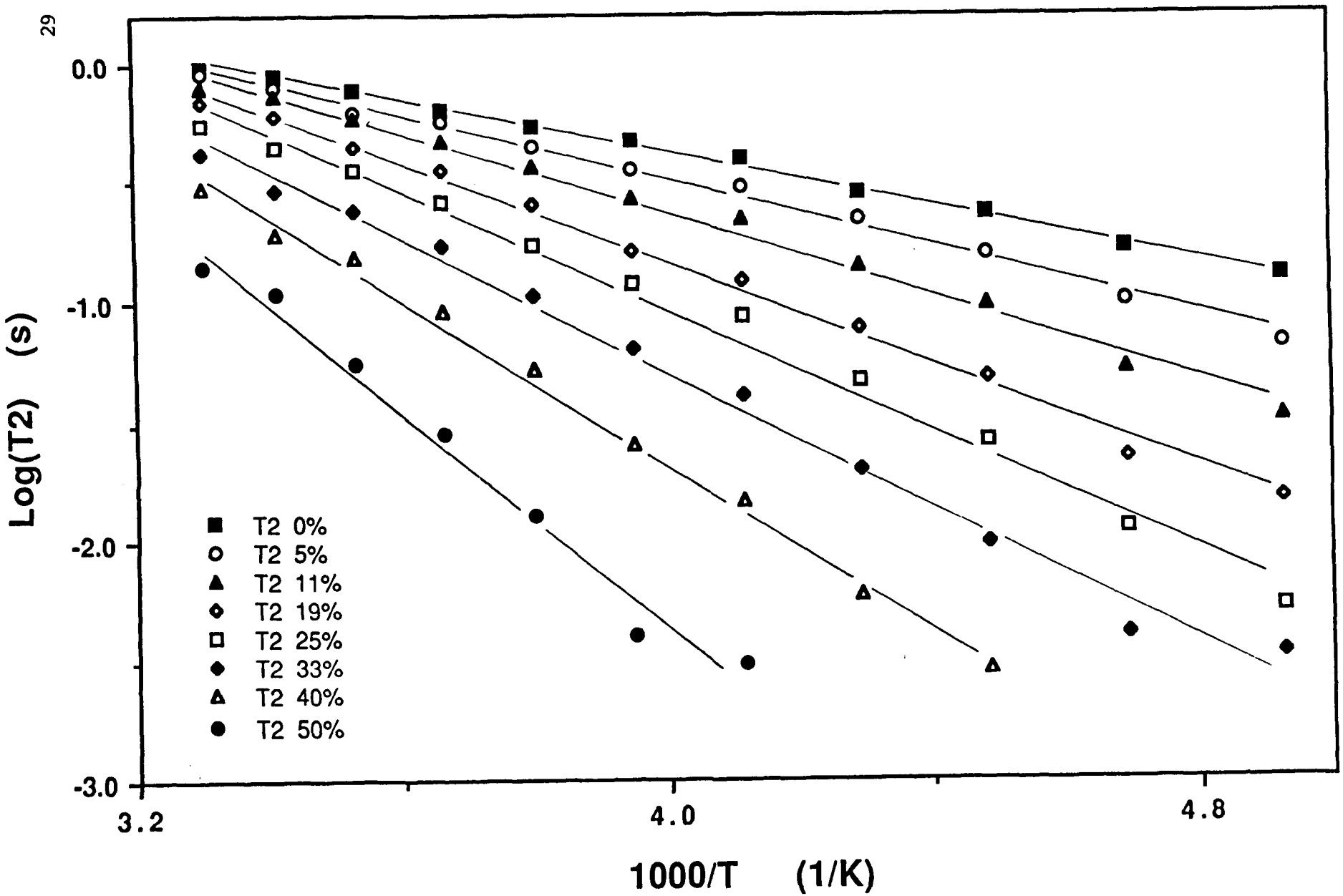

0.0
-1.0
-2.0
-3.0
Log(T2) (s)
3.2
4.0
4.8
1000/T (1/K)
T2 0%
T2 5%
T2 11%
T2 19%
T2 25%
T2 33%
T2 40%
T2 50%

Fig 3

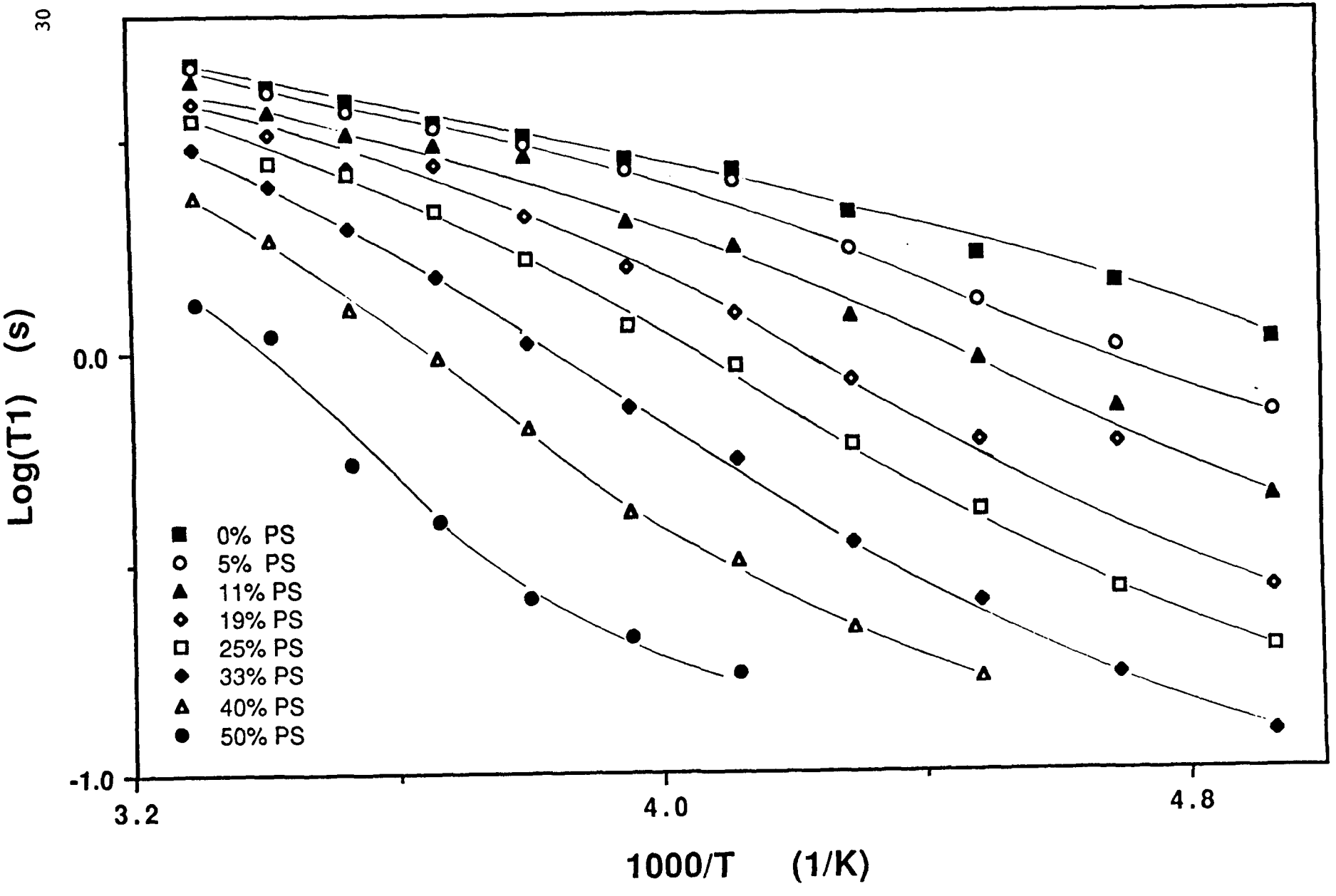

Log(T1) (s)
0.0
-1.0
3.2
4.0
4.8
1000/T (1/K)
0% PS
5% PS
11% PS
19% PS
25% PS
33% PS
40% PS
50% PS

Fig 4

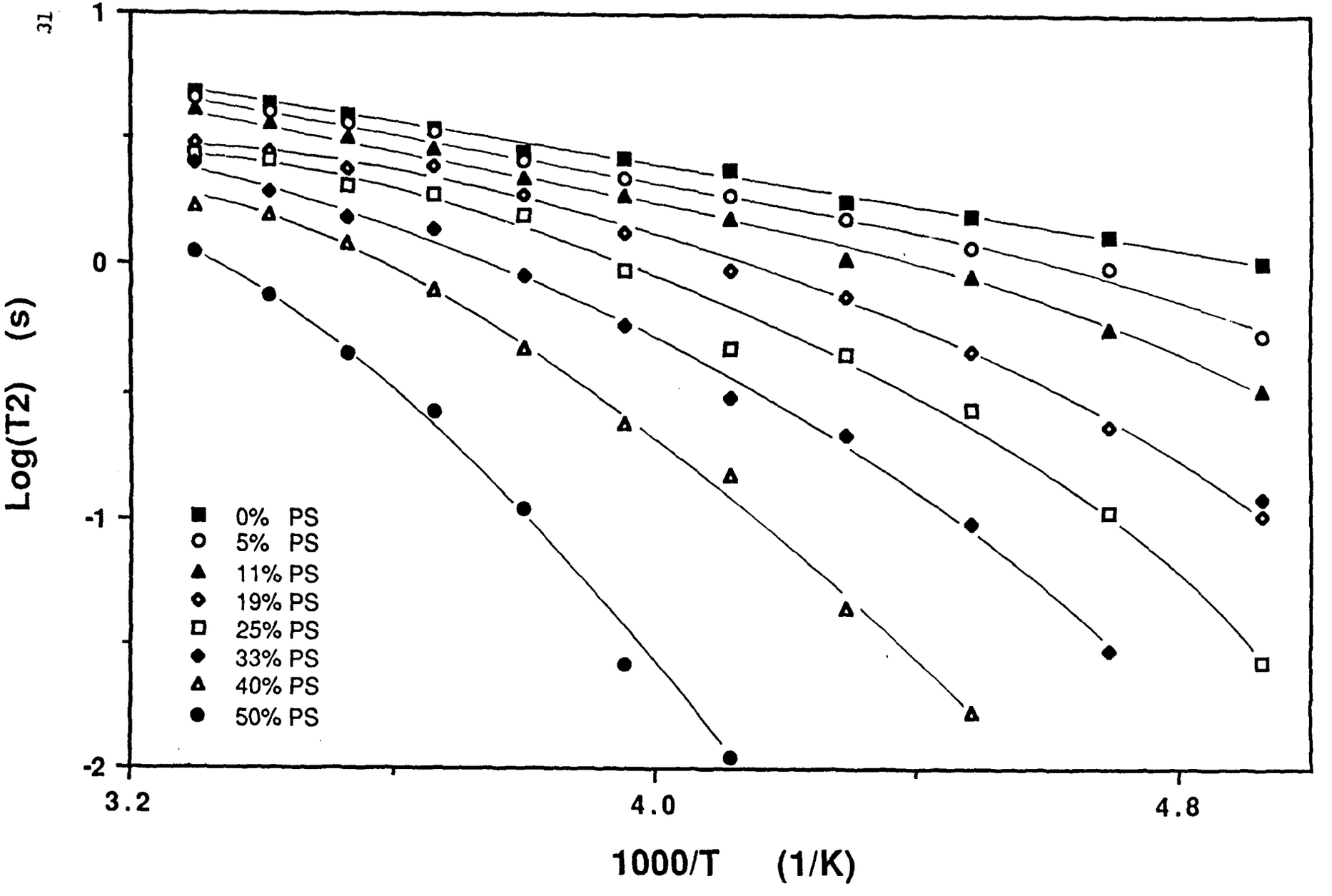

1
0
-1
-2
Log(T2) (s)
3.2
4.0
4.8
1000/T (1/K)
0% PS
5% PS
11% PS
19% PS
25% PS
33% PS
40% PS
50% PS

Fig 5

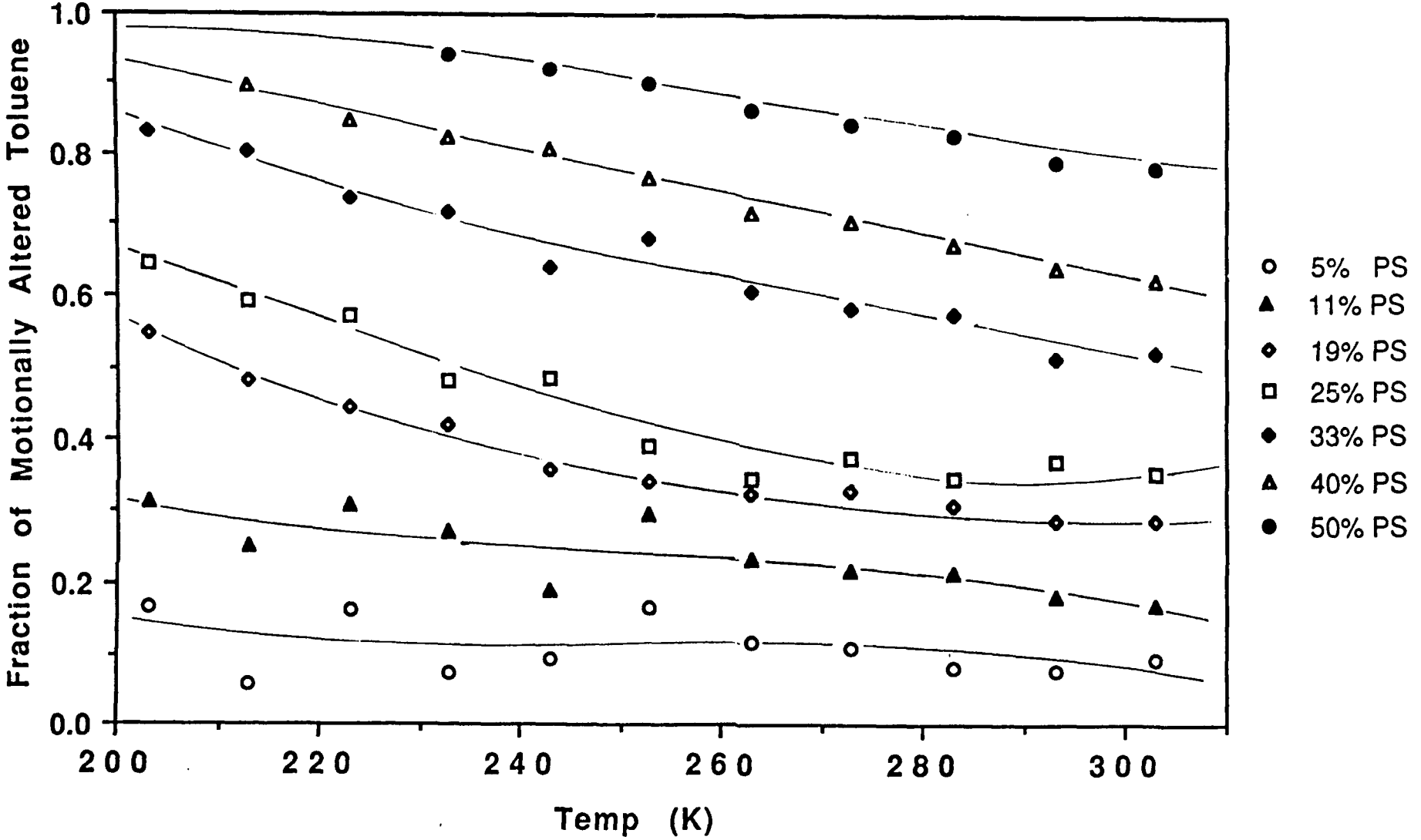

Fraction of Motionally Altered Toluene
1.0
0.8
0.6
0.4
0.2
0.0
200
220
240
260
280
300
Temp (K)
5% PS
11% PS
19% PS
25% PS
33% PS
40% PS
50% PS

Fig 6

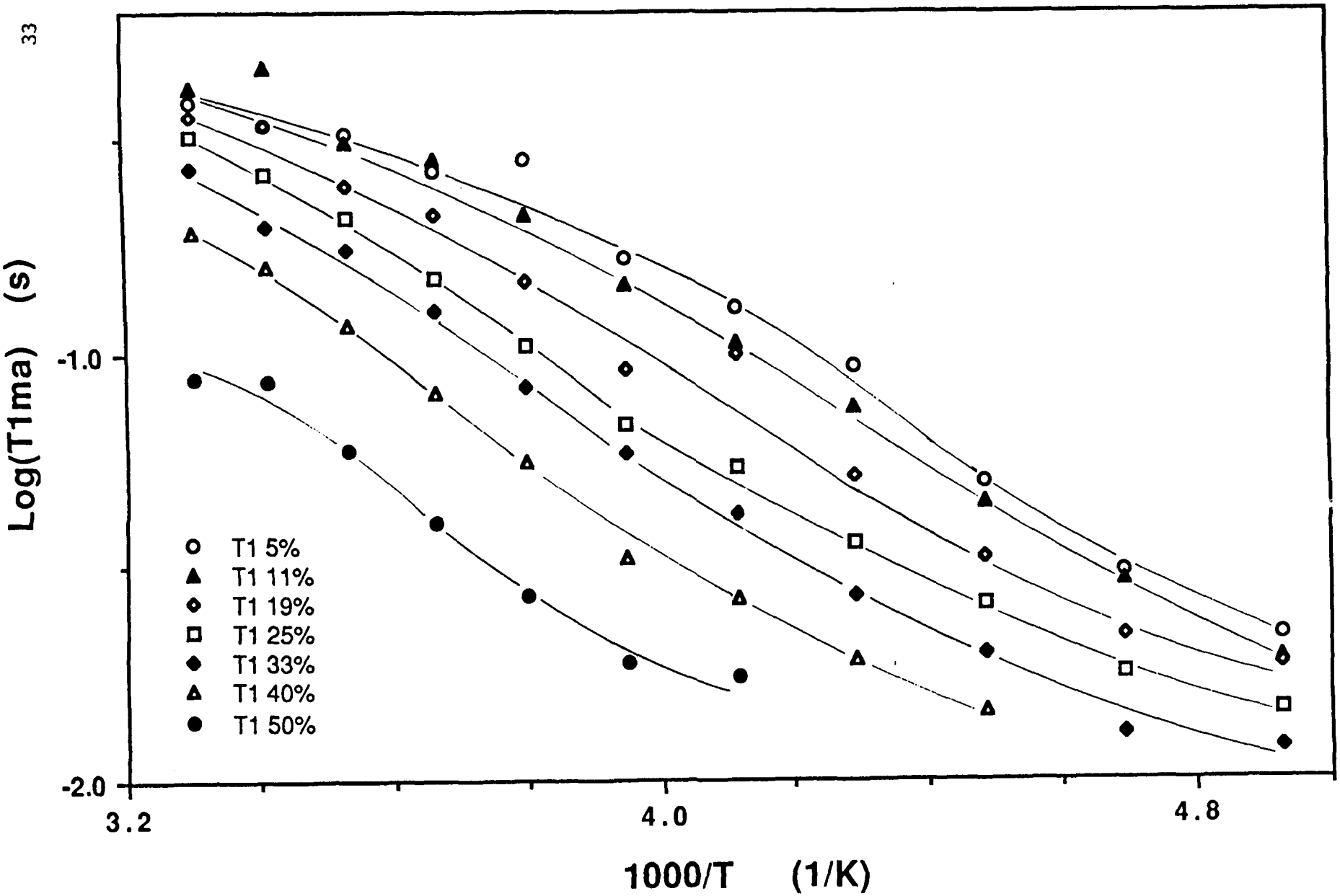

Log(T1ma) (s)
-1.0
-2.0
3.2
4.0
4.8
1000/T (1/K)
T1 5%
T1 11%
T1 19%
T1 25%
T1 33%
T1 40%
T1 50%

Fig 7

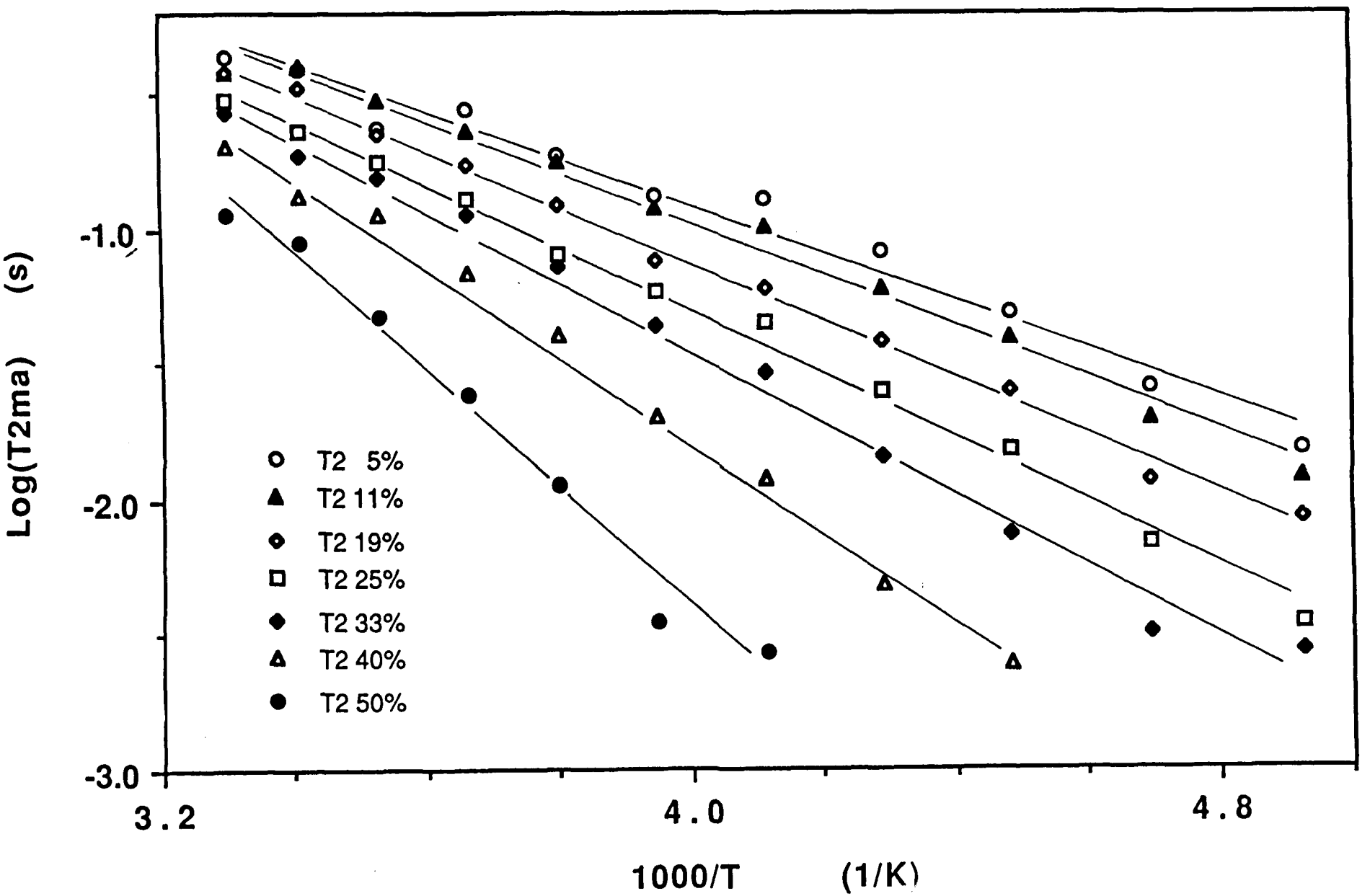

Log(T2ma) (s)
-1.0
-2.0
-3.0
3.2
4.0
4.8
1000/T (1/K)
T2 5%
T2 11%
T2 19%
T2 25%
T2 33%
T2 40%
T2 50%

Fig 8

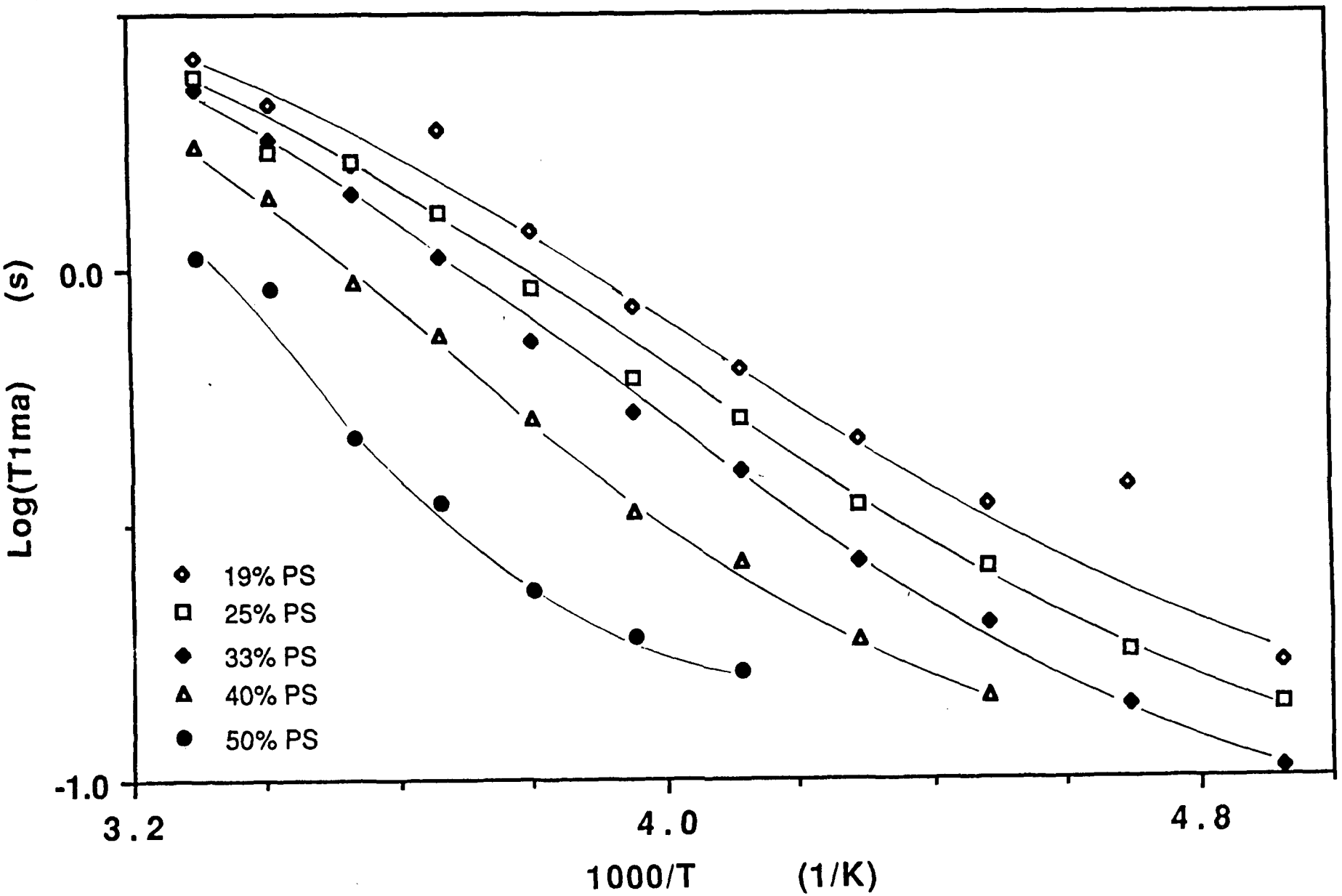


Fig 9

Fig 9

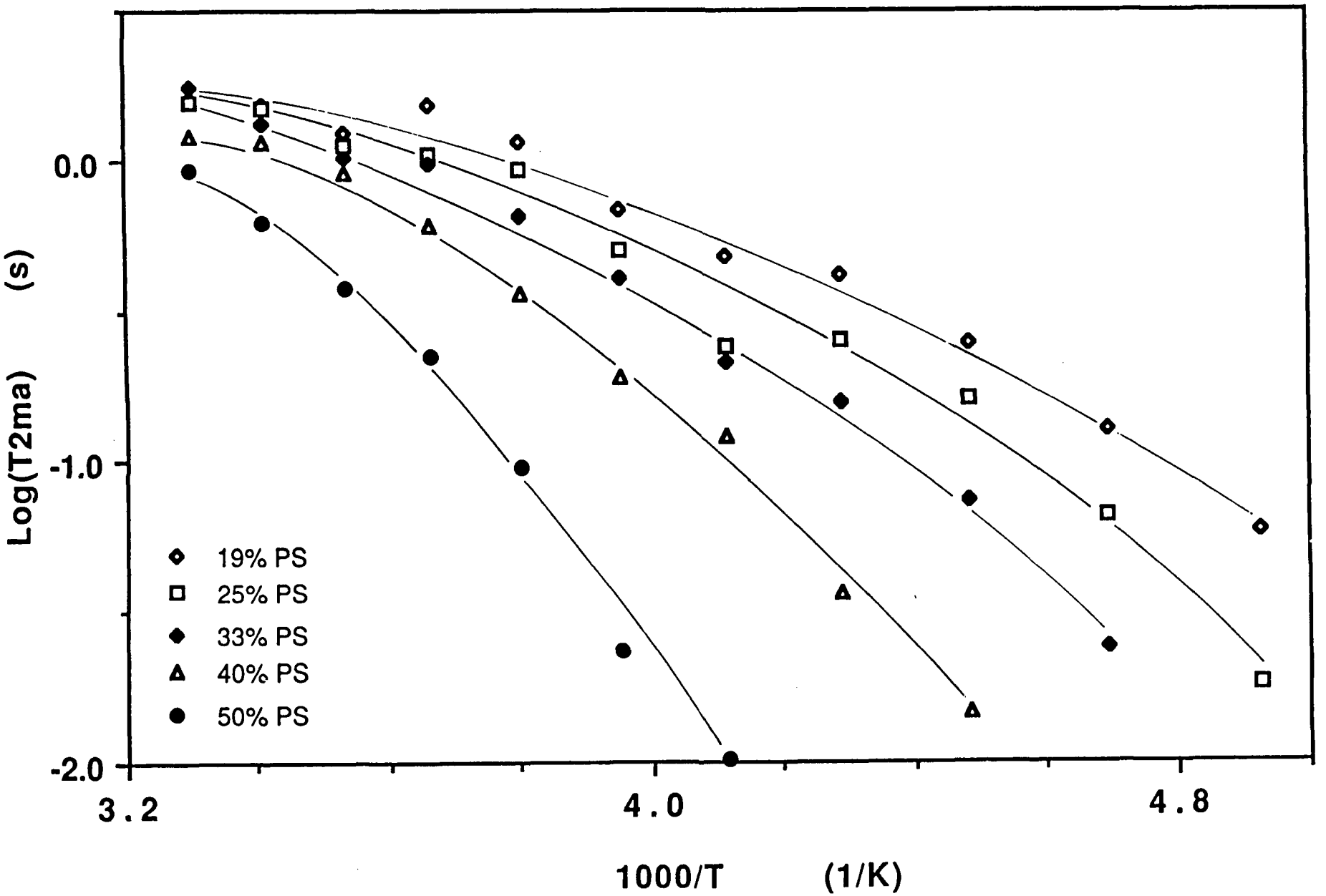


Fig 10

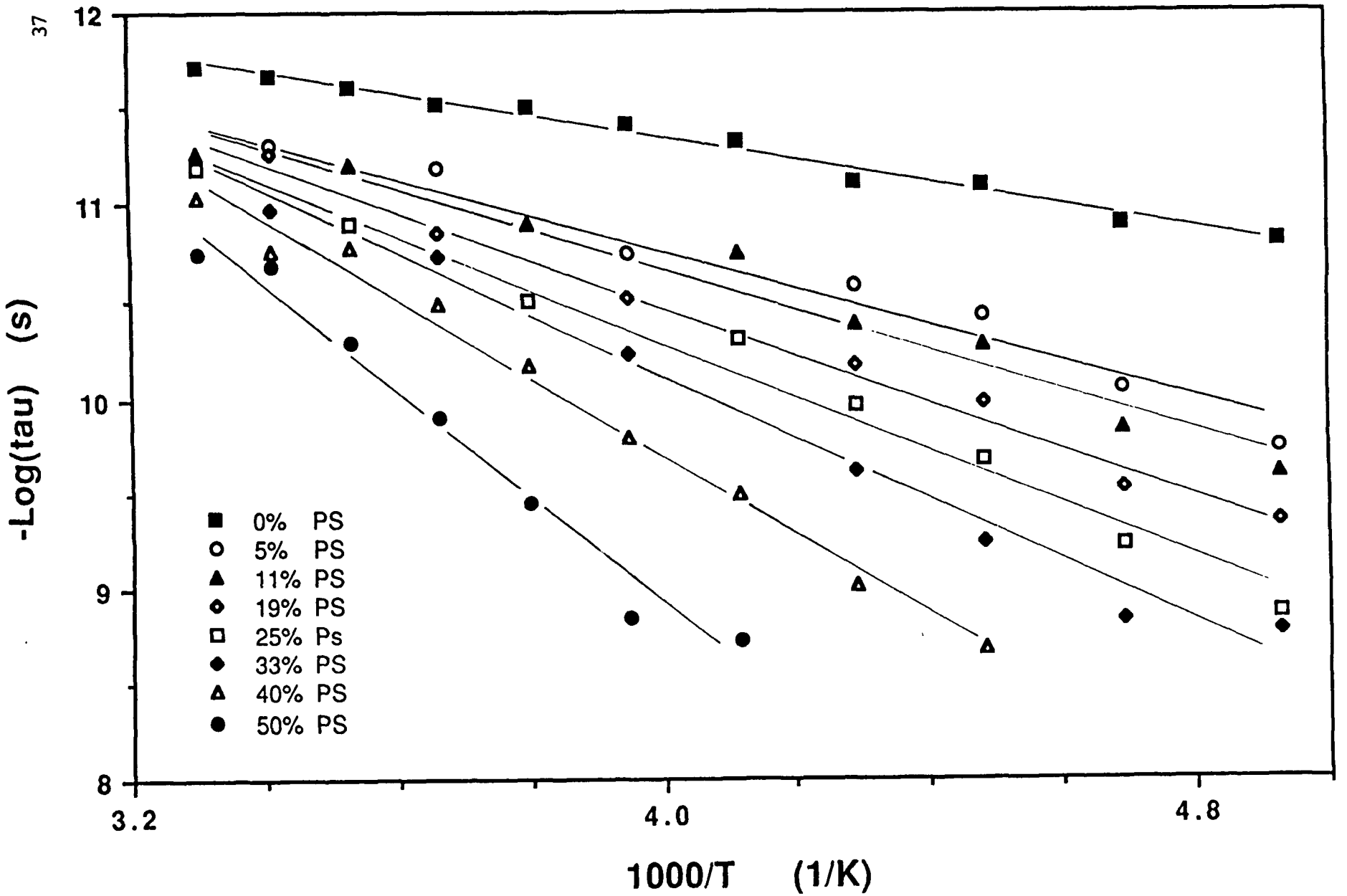

12
11
10
9
8
-Log(tau) (s)
3.2
4.0
4.8
1000/T (1/K)
0% PS
5% PS
11% PS
19% PS
25% Ps
33% PS
40% PS
50% PS

Fig 11